DEVELOPMENT OF NANOCRYSTALLINE IRON-CHROMIUM ALLOY BY MEANS OF SINTERING AND ION IMPLANTATION FOR INTERCONNECT APPLICATION IN HIGH-TEMPERATURE SOLID OXIDE FUEL CELLS

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ABSTRACT

This research is aimed to develop the nanocrystalline iron-chromium (FeCr) alloys by two different sintering methods, spark plasma sintering (SPS) and hot pressing (HP). The sintering temperatures in SPS are designed at 800 and 900 ^{o}C; meanwhile in HP at 1000 ^{o}C. The lower sintering temperature in SPS than HP was carried out in order to obtain the relatively similar in theoretical density of alloy with a minimum grain growth. The alloy has a potential application as interconnector in solid oxide fuel cell (SOFC). The beneficial effect of the reactive element by means of lanthanum (La) into the alloys surface which is introduced using ion implantation is also evaluated. The study focused on the properties, including thermal expansion, oxidation behaviour and electrical resistance of the surface oxide scales. Oxidation testing was conducted at 900-1100 ^{o}C for 100 h in laboratory air. Characterizations by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were carried out before and after each route or process to investigate the microstructure, phase change, and formation of the oxide layer. The specific aspects studied were the effects of nanocrystalline structures, which influenced by the sintering method; and surface treatment through La ion implantation of chromia-forming alloys may improve their high thermal stability. The commercially available ferritic steel is chosen as the comparison with other high-Cr ferritic model alloys. The results revealed that the FeCr alloy prepared by SPS, to be more effective to retain nanocrystalline and better properties than those prepared by HP and commercially available ferritic steel. For all types of materials, the presence of La had no detectable effect on thermal expansion but a major effect on oxide scale adherence. The results consistently showed that better reduction in electrical resistance corresponds with excellent oxidation resistance of the alloy. The performance of FeCr alloy sintered by SPS and implanted by La exhibited the lowest oxidation and electrical resistance of the oxide scale.

ABSTRAK

Penyelidikan ini bertujuan untuk membangunkan besi-kromium (FeCr) aloi *nanocrystalline* dengan dua kaedah pensinteran yang berbeza, *spark plasma sintering* (SPS) dan *hot pressing* (HP). Suhu pensinteran di SPS ditetapkan pada 800 dan 900 ^{o}C; sementara itu, di HP adalah pada 1000 ^{o}C. Suhu pensinteran yang lebih rendah di SPS daripada HP telah digunakan dalam usaha untuk mendapatkan ketumpatan teori aloi yang hampir sama dengan pertumbuhan butiran yang minimum. Ianya mempunyai potensi aplikasi sebagai *interconnector* dalam sel bahan bakar oksida padu (SOFC). Kebaikan penggunaan unsur reaktif iaitu lanthanum (La) ke permukaan aloi yang diperkenalkan menggunakan kaedah implantasi ion juga dikaji. Kajian ini tertumpu kepada sifat bahan iaitu pengembangan haba, pengoksidaan dan penebatan elektrik pada lapisan permukaan oksida. Pengoksidaan ujian dilakukan pada 900-1100 ^{o}C selama 100 jam di ruang udara makmal. Spesimen teroksida ditentukan dengan menggunakan pembelauan sinar-X (XRD), mikroskop pengimbas elektron (SEM) dan tenaga penyebaran sinar-X spektroskopi (EDS) yang dilakukan sebelum dan selepas pada setiap proses untuk mengkaji mikrostruktur, perubahan fasa, dan pembentukan lapisan oksida. Aspek spesifik yang diteliti adalah kesan struktur *nanocrystalline* yang dipengaruhi oleh kaedah sintering; dan rawatan permukaan melalui implantasi ion La dimana ianya dapat meningkatkan sifat kestabilan haba yang tinggi. Keluli feritik komersial dipilih sebagai perbandingan dengan model aloi Cr feritik. Hasil kajian menunjukkan bahawa FeCr aloi menggunakan kaedah SPS lebih efektif dalam mengekalkan sifat *nanocrystalline* berbanding dari yang dihasilkan oleh HP dan keluli feritik komersial. Untuk semua jenis bahan, kehadiran La tidak memberi kesan pada pengembangan haba namun memberi kesan yang besar pada pengikatan oksida. Keputusan yang konsisten menunjukkan bahawa pengurangan rintangan elektrik selari dengan rintangan pengoksidaan pada aloi. Prestasi FeCr aloi yang disinter oleh SPS dan diimplan oleh La menunjukkan pengoksidaan dan rintangan elektrik yang terendah.

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LIST OF SYMBOLS AND ABBREVIATIONS

Ce	-	Cerium
Fe	-	Ferum/Iron
Cr	-	Chromium
FeCr	-	Iron-Chromium
Fe_2O_3	-	Iron Oxide
$(Fe,Cr)_2O_3$	-	Iron Chromium Oxide
Cr_2O_3	-	Chromium Oxide/Chromia
La_2O_3	-	Lanthanum Oxide
$LaCrO_3$	-	Lanthanum Chromite
LaB_6	-	Lanthanum Hexaboride
La	-	Lanthanum
Se	-	Selenium
Ti	-	Titanium
Y	-	Yttrium
ASR	-	Area Specific Resistance
At%	-	Atomic Percentage
CTE	-	Coefficient of Thermal Expansion
Commercial	-	The as-received commercial ferritic alloy
DC	-	Direct Current
EDS	-	Energy Dispersion X-ray spectroscopy
FWHM	-	Full Width at the Half Maximum
h	-	Hour
HP	-	Hot Pressing
HP1000	-	FeCr specimen as ho pressed at 1000 ^oC
ICDD	-	International Centre for Diffraction Data
PDF	-	powder diffraction file
RE	-	Reactive Element

SEM	-	Scanning Electron Microscope
SOFC	-	Solid Oxide Fuel Cell
SPS	-	Spark Plasma Sintering
SPS800	-	FeCr specimen as spark plasma sintered at 800 ^{o}C
SPS900	-	FeCr specimen as spark plasma sintered at 900 ^{o}C
Wt%	-	Weight Percentage
XRD	-	X-Ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

For decades the energy situation in the world has become more and more critical. Conventional energy sources are not sufficient to meet the constantly expanding needs of humanity, so exploration of new energy sources seems to be a challenging task for the future. One possibility for the alternative to conventional energy conversion systems is fuel cell development. Fuel cells are generally regarded to be of central importance for the transformation to the so-called hydrogen economy. These devices offer the impressive potential of efficient generation of power using fuel such as hydrogen with essentially no environmentally harmful by-products. As such, fuel cells have been the focus of many recent research programs (Stover *et al.*, 1999; Wu & Liu, 2010; Zhu & Deevi, 2003a).

One of the most promising and attention fuel cell systems seems to be Solid Oxide Fuel Cell (SOFC) because of its potential for becoming an efficient and high energy-density power generation device (Quadakkers *et al.*, 2003; Steelle, 2001). SOFC development requires the combination of broad groups of different engineering branches. One of the tasks is to invent the most suitable materials for all SOFC components (e.g. anode, cathode, electrolyte and interconnector).

Solid oxides possess sufficiently high ionic conductivity at the elevated temperatures so that SOFC must operate at the temperature range of 800 - 1000 °C. The repetitions of single cells constitute the single stack. However, this structure requires also a mechanical support and a current collector between the different cells to provide a higher voltage and power in a serial connection. Both properties are provided by the interconnector plate. The availability of a suitable material for the interconnector is of key importance for SOFC development. This component is normally a ceramic based material (lanthanum chromite) but there is research trying to develop new interconnector fabricated with metallic alloys (Stöver *et al.*, 1999; Tietz *et al.*, 2002). Metallic materials have the advantage of a higher electronic conductivity, lower cost and easier fabrication than ceramics (Quadakkers *et al.*, 2003). However, the SOFC operating environment is harsh and many common metal alloys are not capable of performing adequately over extended periods. This is especially challenging because the interconnector is exposed to both oxidizing conditions at the cathode and reducing conditions at the anode. This has led to the search for a metal alloy with specific physical and mechanical properties and retains their strength (thermal stability) at the elevated temperatures that could be applied successfully as a fuel cell interconnects.

The metal alloys have long been considered as potential candidates for high temperature applications because their high strength to weight ratio. Among metal alloys in common use, Cr-based alloys and high Cr- ferritic based alloys seem to be the most promising metallic interconnector that forms protective Cr_2O_3 layers upon oxidation at the elevated high temperatures in the air (Quadakkers *et al.*, 2003). This is due to a rather slow growth rate and a proper electric conductivity of the oxide scale (Quadakkers *et al.*, 2003). However, development of the particular ferritic based alloys is a relatively complicated task because the material needs to fulfil several requirements to be suitable as a SOFC interconnector, which sometimes can be even contrary. Based on the requirements in respect to oxidation resistance, the continued growth of oxide scale or oxidation kinetics below 10^{-14} $g^2cm^{-4}s^{-1}$ is required, and a value below 10^{-15} $g^2cm^{-4}s^{-1}$ would be ideal (Antepara *et al.*, 2005), which can lead to the increasing of electrical resistance or lead to the thermal expansion mismatch during thermal cycling in both oxidizing and reducing atmosphere. A large number of ferritic alloys are commercially available in a wide range of compositions; conversely, it seems that none of them can fulfil all requirements for the SOFC interconnector (Quadakkers *et al.*, 2003). Therefore, new FeCr based alloys have recently been developed specifically for SOFC applications. These materials seem to be sufficiently good for most of the envisaged SOFC applications; however, it is still necessary to improve their composition to design alloy, which possesses excellent properties during operation in SOFC relevant atmospheres.

This present study is, in essence, a discussion on designing a nanostrucutred alloy with tailored properties, entirely in the solid state from metal powder precursor. However, the problems arise immediately when trying to manufacture the alloy related to conventional consolidation process, such as in hot pressing (HP). Mainly, due to longer processing times and higher temperature conditions, some grain growth in the structure could not completely be eliminated. When thermal energy is applied to a powder compact, the compact is densified and the average grain size increased. The full-density compacts with retaining nanometric grain size (nanostructured alloy), is of essential significance in interconnector SOFC application, which can produce better properties of alloys, specifically in the reduction the kinetics of oxidation and not easy to achieve. Therefore, in this work the mechanical alloyed Fe-Cr powder had been introduced using spark plasma sintering (SPS) technique to produce the bulk FeCr alloy, since this process is capable of control of producing many metallic alloys with a perfectly controlled degree of densification and microstructure with near theoretical density over 99 % at relatively lower sintering temperature (200 to 500 ^{o}C) than temperature used in conventional HP process (Omori, 2000). In spite of that, this method also cost effective sintering and can be completed in a short period of approximately 5 to 20 minutes including temperature rise and holding times (Omori, 2000). In particular, it is essential to compare these two sintering process, SPS and HP, in order to demonstrate the effectiveness of these approaches in improving the high temperature properties of the sintered alloy which would be of significant in practical importance, specifically in SOFC interconnector.

The use of controlled surface modification is a viable alternative to reduce oxidation rates and extend the useful life of a potential alloy as interconnects in SOFC. Ion implantation is a physical method for the modification of surface properties of materials by insertion of accelerated atoms, within the first atomic layers into solid substrates (Marest, 1998). As a process, ion implantation is widely used to modify the oxidation behaviour to the surface of the alloys. Modification of the corrosion behaviour of metal surfaces by ion implantation will allow the introducing of a controlled reactive element (RE) concentration into the alloys surface. It has been known that the minor addition of RE, such as La, Y, Ti, Hf, and Ce, could significantly improve the spallation resistance of these oxide scales under oxidising and/or reducing conditions and inhibits further by isothermal and thermal cycling oxidation (Cooper *et al.*, 2008). This implantation on the surfaces of the Fe-Cr alloys may help mitigate chromium volatility, reduce the oxide scale growth rate of the chromia-forming alloy which can lead to the formation of phase that may increase the electrical resistance or lead to the thermal expansion mismatch during thermal cycling. In this research, the investigation, the beneficial effect of La ion implantation on the oxidation behaviour of alloys also is considered.

The main emphasis of this study was made to investigate the effect of each process in the high temperature oxidation resistance in the temperature range required for SOFC application (800 - 1000 °C). The scale formation mechanisms in the case of the most promising materials were investigated during oxidation times up to 100 hours and the influence of minor RE addition, specifically La, trough surface treatment - ion implantation in the alloy was also elaborated. For a better understanding of the mechanisms of oxidation for Fe-Cr alloy, the available high-Cr ferritic model alloys were prepared and incorporated into the test program. Characterisations by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) was carried out to investigate the microstructure, phase change, and formation of the oxide layer. The electrical conductivity of the interconnector is a crucial property for SOFC application whereby the conductivity of the chromia based oxide scale formed on the metallic surface during stack operation has to be taken into account in the overall conductivity value. Nevertheless, the thermally grown oxide scale of the alloy may overgrow during operating temperature, resulting in scale spallation due to the thermal stress may occur in the alloys, which induced by the thermal expansion mismatch between the scale and substrate. Due to these issues, dilatometry studies were conducted to observe the thermal expansion behaviour of metal alloys which predict these values as a function of temperature is also the very important fundamental parameter in SOFC application.

1.2 Problem Statement

The identification and fabrication of suitable interconnector materials are a major challenge in the development of SOFC. Iron-Chromium or FeCr alloys have received considerable attention as potential interconnector materials due to high strength and thermal stability. However, the problems arise immediately when trying to manufacture the nanostructured FeCr alloy whereby steps must be taken to avoid the grain growth during solidification, which can influence to the improved properties of alloys, specifically in oxidation resistance and this is not easy to achieve. Thus, the temperature and time of consolidation have to be restricted at low value to keep the nanofeatures by using the advance consolidation process - spark plasma sintering with respect to microstructural and smaller grain size control. On the other hand, they may fail through loss of strength or gradually deteriorate with the surrounding atmosphere during SOFC operating temperature. Therefore, the formation of a stable oxide layer through ion implantation is required to protect the underlying materials.

1.3 Objectives of Study

The main objective of the present work is to develop the nanostructured FeCr alloy using sintering and ion implantation for SOFC temperatures environment application. In order to achieve this, several sub-objectives are withdrawn:

i. To develop nanostructured FeCr alloys by using spark plasma sintering method in order to reduce and control the grain growth of alloys.

ii. To investigate the different sintering process, SPS and HP, in improving thermal stability of nanostrucutred FeCr alloy in terms of properties: thermal expansion, oxidation behaviour and electrical resistance.

iii. To determine the effect of lanthanum ion implantation on the FeCr alloys microstructure and oxidation behaviour at 900, 1000 and 1100°C.

iv. To compare the as developed FeCr alloy with the commercial alloy in terms of the investigated properties.

v. To obtain the best method of developing novel FeCr based alloy for high temperature application, specifically interconnector SOFC material, based on the results analyzed.

1.4 Scopes of Study

The scopes of this research include the following aspects:

i. Development of nanostructured FeCr alloys by using SPS sintering method and compared with conventional HP sintering process.

ii. Surface treatment via ion implantation with doses of lanthanum ion of 1×10^{17} ions/cm^2.

iii. Thermal expansion test by using push rod dilatometer-thermo mechanical analyzer between room temperature and 900 ^{o}C.

iv. Cyclic oxidation test at 900, 1000 and 1100 °C for 100-hours oxidation times.

v. Electrical resistance test of the oxidized sample by using the two point probe method.

vi. Microstructure and phase analysis before and after the implementation of ion implantation and cyclic oxidation by using Scanning Electron Microscope (SEM), Energy Dispersion X-ray Spectroscopy (EDS), and X-Ray Diffraction analysis (XRD).

vii. Determination of the optimum way of developing FeCr based alloy with and without lanthanum ion implantation and different consolidation technique for high temperature application as fuel cell interconnector based on the results analyzed.

CHAPTER 2

LITERATURE REVIEW

2.1 Solid Oxide Fuel Cell

Solid oxide fuel cells (SOFC) are devices that generate electricity from the electrochemical conversion of a fuel and oxidant (Minh, 1993). A simplified configuration and operating principle of an SOFC using hydrogen as fuel is shown in Figure 2.1. A basic fuel cell comprised of three components: an electrolyte sandwiched between two electrodes (an anode and cathode). Under operating conditions, fuel enters and is oxidized at the anode portion of the cell, liberating electrons. Electrical power is produced as electrons flow from the anode to the cathode. Oxidant on the cathode side accepts electrons and is reduced to an ionic species. The circuit is completed by the diffusion of oxidant ions through the electrolyte. In practice fuel cells are not used individually, but in modular stacks where a fourth component-an electrical interconnect joins the individual cells. Since the reactants are often in the gaseous state, the interconnect usually serves to separate fuel and oxidant as well, thus preventing the fuel and oxidant gases from mixing. The interconnect is sometimes designated the bipolar plate, or separator, emphasizing the different polarities of anode and cathode which it connects or the gas separation, respectively.

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